189. *Electron-transfer Reactions between Oxygen and Aromatic Hydrocarbons.*

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The reversible formation of the perylene monopositive ion from perylene and molecular oxygen in solutions of varying acidity in the presence of oxygen up to 100 atm. has been investigated. The monopositive ion is not formed in acetic acid, but is readily formed in trifluoroacetic acid in contact with air.

The equilibrium was studied in mixtures of trifluoroacetic and acetic acid. It appears that the oxygen molecule takes up one electron and that an ion pair $M^{+}\cdot O_2^{-}$ (M = perylene) is formed. It is estimated that the average life-time of the complex in $CF_3\cdot CO_2H$ is about 10^{-7} sec.

The change of line shape and the loss of hyperfine structure of the electron-spin resonance spectrum of the perylene positive ion in solutions of different acidity and viscosity, and the influence of oxygen, were investigated. The broadening of the spectrum in $CF_3\cdot CO_2H$ is in agreement with an electron transfer with a frequency of about 10^7 sec.$^{-1}$.

In a previous paper [1] it was reported that the proton complexes of strongly basic aromatic hydrocarbons can be transformed into their monopositive ions when brought into contact with molecular oxygen. The reaction appeared to be reversible. However, the nature of the compounds formed from oxygen remained unexplained.

The effect of the oxygen pressure on the equilibrium between the perylene molecule and its monopositive ion in a weak acid has now been studied.[2]

Experimental

The apparatus for handling solutions in hydrogen fluoride as well as the high-pressure absorption cell have been described elsewhere.[2] A Cary model 11 spectrometer was used for recording the ultraviolet spectra.

The electron-spin resonance (E.S.R.) spectra were measured with a Varian V 4500 spectrometer, which operates at a nominal frequency of 9400 Mc./sec. A 6-inch magnet was used. The magnetic field, which was modulated with a frequency of 100 kc./sec., was determined with a precision gaussmeter model M 2 of Nuclear Magnetics Corporation.

The electron-spin resonance spectrum of perylene in hydrogen fluoride has been measured by using a probe made of Teflon of 0·8 mm. internal and 5 mm. external diameter. Even with this small internal diameter the high dielectric loss of hydrogen fluoride caused a significant decrease in the quality factor of the cavity.

The spectra at low temperature were measured by insertion of a vacuum-jacketed Dewar glass tube in the cavity; the quality of the cavity decreased considerably and relatively poor spectra were obtained.

The chemicals were of the same source as previously.[1] Nitric oxide (Matheson Inc.) was used without further purification.

Results

The experiments with various hydrocarbons M in strong acids indicated that in the presence of oxygen an equilibrium exists between proton complex MH^+ and monopositive ion M^+.[1] * In this reaction an electron is transferred from the hydrocarbon to the oxygen molecule, but whether oxygen takes up one or two electrons remained uncertain.

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* Nitric oxide in acidic solutions can also act as an electron-acceptor. At small pressures ($\ll 1$ atm.) it converts the proton complexes of 3,4-benzopyrene and pyrene in hydrogen fluoride into their monopositive ions. At higher pressures (2 atm.) 1,2-benzanthracene is almost completely converted into its positive ion, which indicates that nitric oxide is a better acceptor than oxygen in hydrogen fluoride. The reactions with nitric oxide were not further investigated.

[1] Aalbersberg, Hoijtink, Mackor, and Weijland, *J.*, 1959, 3049.

[2] Cf. Aalbersberg, Thesis, Free University, Amsterdam, 1960.

An attempt to establish the reaction equation by spectroscopic determination of the ratio $[M^+]/[MH^+]$ failed because the conversion of the proton complexes of perylene and tetracene into their monopositive ions is nearly quantitative even at low oxygen pressures, whereas the proton complexes of other hydrocarbons studied decompose or form precipitates at higher oxygen pressures.

Absorption Spectra.—Fig. 1 shows that the stability of the positive ion decreases at lower acidity of the solvent. In $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (29 mole % of complex; $H_0 = -9{\cdot}22$; cf. ref. 1) perylene is converted nearly quantitatively into the monopositive ion on contact with air (Fig. 1a), whereas a solution of perylene in acetic acid–benzene (89 : 11 v/v) is stable even at 30 atm. oxygen pressure (Fig. 1e).

FIG. 1.

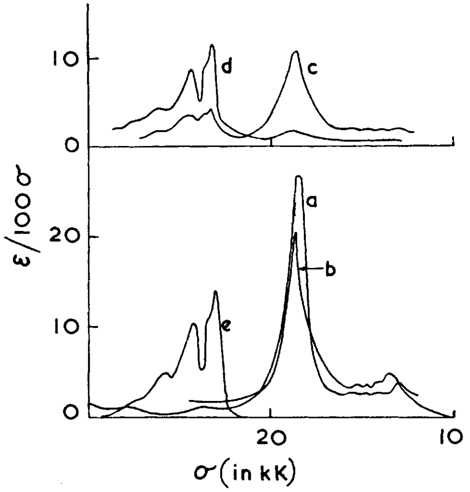

FIG. 2.

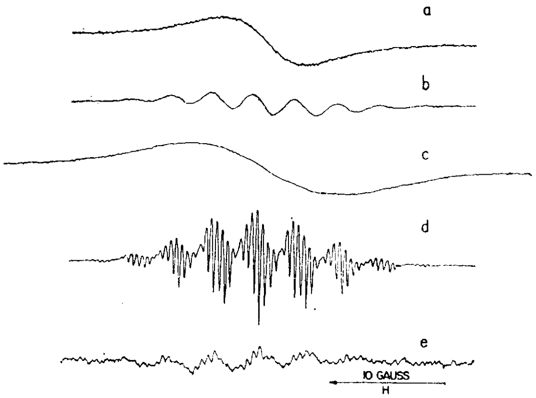

FIG. 1. *Absorption spectra* (20°) *of perylene in*: (a) $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (29 *mole* % *of complex*) *after contact with air*; (b) $CF_3{\cdot}CO_2H{-}C_6H_6$ (89 : 11 v/v) *at* 4 *atm. oxygen pressure*; (c) $CF_3{\cdot}CO_2H{-}AcOH{-}C_6H_6$ (57 : 32 : 11 v/v) *at* 60 *atm. oxygen pressure*; (d) $CF_3{\cdot}CO_2H{-}AcOH{-}C_6H_6$ (57 : 32 : 11 v/v) *after contact with oxygen* (60 *atm.*) *and expansion*; *and* (e) $AcOH{-}C_6H_6$ (89 : 11 v/v) *at* 30 *atm. oxygen pressure.*

FIG. 2. *Derivatives of electron-spin resonance spectra of perylene in*: (a) HF *at* 20° *after contact with air*: (b) $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (40 *mole* % *of complex*) *at* 20° *after contact with air*; (c) *in* $CF_3{\cdot}CO_2H$ *after contact with air*; (d) *in* 98% H_2SO_4; *and* (e) *in* $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (40 *mole* % *of complex*) *at* −30° *after contact with air.*

The formation of this ion was quantitatively studied in trifluoroacetic–acetic acid–benzene (57 : 32 : 11 v/v). In this medium perylene dissolves as a molecule and high oxygen pressures are needed to convert it into its monopositive ion (Fig. 1c).*

The formation of the positive ion from perylene and oxygen is rapid. The absorption spectra of the solutions slowly change, the absorption bands of the molecule as well as of the positive ion decreasing in intensity. After lowering of the pressure to 1 atm. the solutions mainly display the absorption bands of the molecule (Fig. 1d). When this procedure was performed rapidly, at least 85% of the perylene initially dissolved could be recovered. The results are summarized in Table 1. The concentration of the positive ion has been taken as the difference between the concentration of molecule present initially and after admission of oxygen, as calculated from the absorption spectrum.

Electron-spin Resonance Spectra.—The electron-spin resonance spectra of perylene, dissolved in anhydrous $HF{-}CF_3{\cdot}CO_2H{-}H_2O,BF_3$ (40% of complex) and trifluoroacetic acid after contact with air, as well as in sulphuric acid, are given in Fig. 2. The hyperfine structure of the perylene

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* Benzene was added to the acidic solvent to dissolve perylene to a sufficient extent. This has the disadvantage of lowering the molar extinction coefficients of the bands of the positive ion somewhat (cf Figs. 1a and b).

TABLE 1. *Concentration of molecule* [M] *and positive ion* $[\mathrm{M}^+]$ *and the ratio* $[\mathrm{M}^+]/[\mathrm{M}]$ *in a solution of perylene in* $\mathrm{CF_3{\cdot}CO_2H{-}AcOH{-}C_6H_6}$ (57 : 32 : 11 *v/v*) *at* 20° *and various oxygen pressures.*

(Concns. are 10^{-4} mole $\mathrm{l.}^{-1}$.)

p (atm.)	[M]	$[\mathrm{M}^+]$	$[\mathrm{M}^+]/[\mathrm{M}]$	p (atm.)	[M]	$[\mathrm{M}^+]$	$[\mathrm{M}^+]/[\mathrm{M}]$	p (atm.)	[M]	$[\mathrm{M}^+]$	$[\mathrm{M}^+]/[\mathrm{M}]$
0	1·09	0·11	0·10	30	0·40	0·80	2·00	80	0·20	1·10	5·50
9½	0·66	0·54	0·82	36	0·37	0·83	2·24	85	0·21	1·09	5·20
12	0·60	0·60	1·00	43	0·35	0·85	2·43	95	0·16	1·04	6·50
18½	0·49	0·71	1·45	60	0·26	1·04	4·00	95	1·19 *	6·01 *	5·05
24	0·45	0·75	1·67								

* At this high concentration the perylene is decomposed rapidly. Only 35% of the amount initially dissolved could be recovered after elimination of the oxygen.

TABLE 2. *Electron-spin resonance spectra of the perylene positive ion in different acids.*

Fig. 2	Solvent	Shape	Total width * in gauss	Viscosity in poise	$\langle \Delta H^2 \rangle$ in gauss ^{2}
a	HF at 20°	One line	29	0·002	34
b	$\mathrm{CF_3{\cdot}CO_2H{-}H_2O{-}BF_3}$ (40%) at 20° c	9 lines of *ca.* 3·5 gauss each	29	0·08	35
c	$\mathrm{CF_3{\cdot}CO_2H}$ at 20°	One line	41	0·008	49
d	$\mathrm{H_2SO_4}$ † at 20°	59 lines of *ca.* 0·51 gauss each	30	0·24	30
e	$\mathrm{CF_3{\cdot}CO_2H{-}H_2O,BF_3}$ (40%) at −30° c	59 lines of *ca.* 0·51 gauss each	30	0·45	—
—	$\mathrm{H_2SO_4{-}H_3PO_4}$ (2 : 3 v/v) at 55° c	59 lines of *ca.* 0·51 gauss each	30	0·15	—
—	$\mathrm{H_2SO_4{-}H_3PO_4}$ (2 : 3 v/v) at 20·5° c	45 lines of *ca.* 0·51 gauss each	25	0·52	—
—	$\mathrm{H_2SO_4{-}H_3PO_4}$ (2 : 3 v/v) at −14° c	7 lines of *ca.* 3·5 gauss each	25	3·15	—

* Total width has been measured between the points where the resonance signal could just be distinguished from the noise. † The g-value of the ion in sulphuric acid is 2·0028.[3b]

positive ion in sulphuric acid appears to be well resolved.[3] The spectrum was measured at a micro-wave energy level considerably lower than normally applied. At higher energy saturation broadening of the hyperfine structure [4] was observed. The spectra of the perylene positive ion in the other acids were measured at the energy level used for the sulphuric acid solution. It can be seen that the shape and the width differ considerably, and that a better resolution of the hyperfine structure for perylene in $\mathrm{CF_3{\cdot}CO_2H{-}H_2O,BF_3}$ is obtained at −30° c (see also Table 2).

In addition, the spectrum was measured in a 2 : 3 v/v oxygen-free mixture of sulphuric and phosphoric acid at 55°, 20·5°, and −14° c (Table 2). At 55° the resolution obtained was similar to that in sulphuric acid, but at lower temperature the hyperfine structure is not fully resolved and at −14° c the spectrum resembles that of Fig. 2b. Evidently in the absence of oxygen and at high viscosities (estimated correlation time for rotation $\sim 10^{-8}$ sec.) the anisotropy of the hyperfine interaction results in a broadening of the spectrum.[5]

In highly acidic solvents of low viscosity in the presence of oxygen ($\sim 5 \times 10^{-3}$ mole $\mathrm{l.}^{-1}$) there is again loss of hyperfine structure. This is attributed to exchange between oxygen and the perylene positive ion.[5,6,7] The exchange interaction becomes less at higher viscosities, as can be seen by comparing Figs. 2a, b, and e.

DISCUSSION

Evans [8] has shown that in chloroform weak complexes are formed between oxygen or nitric oxide and aromatic hydrocarbons. These complexes display well-defined absorption

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[3] (*a*) de Boer and Weissman, *J. Amer. Chem. Soc.*, 1958, **80**, 4549; (*b*) de Boer, Thesis, Free University, Amsterdam, 1958; (*c*) Carrington, Dravnieks, and Symons, *J.*, 1959, 947.

[4] Lupinski, Thesis, Leiden, 1959.

[5] Pake and Tuttle, jun., *Phys. Rev. Letters*, 1959, **3**, 423.

[6] Deguchi, *J. Chem. Phys.*, 1960, **32**, 1584.

[7] Hausser, *Naturwiss.*, 1960, **47**, 251.

[8] Evans, *J.*, 1957, 1351, 3885.

bands of the singlet–triplet transitions of the hydrocarbons. The optical density is approximately proportional to the oxygen pressure, which suggests the reaction

$$\mathrm{M + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M,O_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Hoijtink [9] explained these singlet–triplet transitions on the basis of exchange interaction in the complexes. That these weak complexes may have a certain stability is clear from the charge-transfer-type absorption bands observed.

Our results show that greater acidity of the solvent favours electron-transfer, leading to the formation of the positive ions M^+. In solvents of relatively low acidity our results are consistent with the reaction

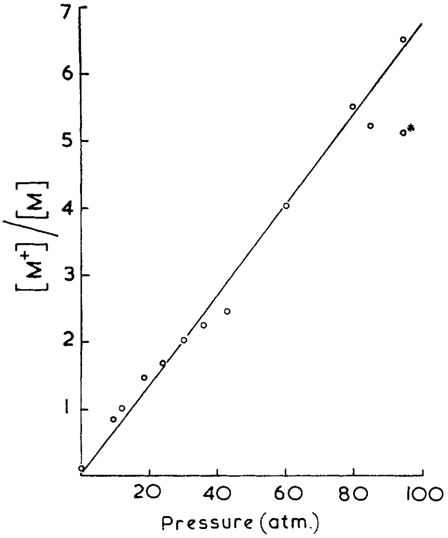

FIG. 3. *Ratio* $[M^+]/[M]$ *as a function of the oxygen pressure for perylene in* $CF_3 \cdot CO_2H$–AcOH–C_6H_6 (57 : 32 : 11 v/v). (*For point marked * see footnote to Table* 1.)

$$\mathrm{M + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M^{+} \cdot O_2^{-}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in other words, with an electron-transfer in the complex M,O_2:

$$\mathrm{M,O_2 \rightleftharpoons M^{+} \cdot O_2^{-}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In solvents of higher acidity and higher dielectric constant, for example, anhydrous hydrogen fluoride, the complex will dissociate and probably give rise to hydrogen peroxide:*

$$\mathrm{2M + O_2 + 2HF \rightleftharpoons 2M^{+} + 2F^{-} + H_2O_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It is the increase in acidity rather than an increase in dielectric constant that leads to electron transfer in M,O_2.†

Absorption Spectra.—Reaction (2) requires that the ratio $[M^+]/[M]$ should increase linearly with the oxygen pressure and be independent of the concentration of hydrocarbon. Fig. 3 shows that these requirements are met by the experimental results. The equilibrium constant, defined as

$$K' = \frac{[M^{+} \cdot O_2^{-}]}{[M]p} \quad \text{or} \quad K = \frac{[M^{+} \cdot O_2^{-}]}{[M][O_2]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

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* It is indeed difficult to obtain solutions of the proton complex of perylene in hydrogen fluoride because traces of oxygen will convert it into the positive ion. At atmospheric pressure of oxygen the ratio $[M]/[M^+]$ is estimated to be of the order of 10^{-7}.

† A solution of perylene in methanol at 45 atm. of oxygen did not display the bands of the positive ion.

[9] Hoijtink, *Mol. Phys.*, 1960, **3**, 67.

where p is the partial pressure of oxygen, is given by $K' = 0{\cdot}067$ atm.$^{-1}$ or $K = 5$ l. mole^{-1}. Evidently the electron-transfer complex $M^+{\cdot}O_2^-$ in this medium is very weak and readily dissociates into the hydrocarbon and oxygen. The average life-time can be estimated in the following manner: the rate k_1 of reaction (1) between the uncharged partners, perylene and oxygen, will be diffusion-limited. This is consistent with the observation that the quenching by oxygen of the fluorescence of aromatic molecules in acetic acid is diffusion-limited. If we assume that the electron-transfer of reaction (3) is fast, the rate constant k_2 of reaction (2) is also diffusion-limited and therefore of the order of 10^{10} sec.$^{-1}$ l. mole^{-1}. Thus, since the equilibrium constant $K = 5$ l. mole^{-1}, the rate constant k_{-2} must be approximately equal to 10^9 sec.$^{-1}$, which means that the average life-time of the complex is of the order of 10^{-9} sec. If, however, the electron-transfer is slow, or if it only occurs when the aromatic molecule and the oxygen molecule are in a particular conformation, the average life-time will be greater.

The values of the constant K for various acid mixtures given in Table 3 illustrate the influence of the acidity. In trifluoroacetic acid the average life-time of the complex must be $\sim 10^{-7}$ sec. if one assumes the reaction to be diffusion-limited.

TABLE 3. *Values of the equilibrium constant K (l. mole^{-1}) of reaction (2) for various acid mixtures at 20°.*

Composition (v/v) of acid mixture	K	Composition (v/v) of acid mixture	K
$CF_3{\cdot}CO_2H{-}C_6H_6$ (89 : 11)	$\sim 10^3$	$CF_3{\cdot}CO_2H{-}AcOH{-}C_6H_6$ (70 : 19 : 11)	$\sim 4 \times 10^2$
$AcOH{-}C_6H_6$ (89 : 11)	$<2 \times 10^{-2}$	,, ,, (57 : 32 : 11)	5
		,, ,, (44·5 : 44·5 : 11)	$\sim 2 \times 10^{-1}$

Electron-spin Resonance Spectra.—The question arises if one can deduce from the electron-spin resonance spectra whether electron-transfer occurs in the complex $M^+{\cdot}O_2^-$, for which an average life-time of 10^{-7} sec. was calculated. For this purpose the spectra of the perylene positive ion in anhydrous hydrogen fluoride and $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ will be compared with that in trifluoroacetic acid. In the former strongly acidic solvents one does not expect electron-transfer since the complex $M^+{\cdot}O_2^-$ is completely dissociated, but the exchange interaction with the oxygen molecule causes a loss of structure, which loss, in accordance with the results in Table 2, decreases with increasing viscosity.[5] For the latter process one expects the second moment $\langle \Delta H^2 \rangle$ of the spectrum to be approximately constant. Table 2 shows this to be the case. If the argument of Pake and Tuttle[5] is used, the line width of 7·6 gauss of the spectrum in hydrogen fluoride (Fig. 2a) leads to a frequency of the phase-interrupting collisions between oxygen and the perylene positive ion of 10^7 sec.$^{-1}$. This value may be compared with the frequency of collisions between proton complexes and oxygen in hydrogen fluoride that produce quenching of the fluorescence of the former. The frequency of these collisions under comparable conditions was found[10] to be 5×10^7 sec.$^{-1}$, from which it appears that the exchange process is efficient.

The second moment of the spectrum of a solution in trifluoroacetic acid is significantly greater: 49 gauss^2 as compared with 35 gauss^2. This broadening of the spectrum can be interpreted as caused by an electron-transfer in the complex at a rate of about 10^7 sec.$^{-1}$, which agrees with the estimate given above.

In strongly acidic solvents one expects oxygen to form hydrogen peroxide according to reaction (4). In accordance with this, the electron-spin resonance spectra of these solutions give no indication of any other paramagnetic particle. Further the hyperfine structure of the spectrum of the perylene positive ion in these solutions is much better resolved when the frequency of the phase-interrupting collisions between oxygen and the perylene positive ion is decreased by increasing the viscosity, *e.g.*, in a solution of $CF_3{\cdot}CO_2H{-}H_2O,BF_3$ at $-30°$ C (Fig. 2e). Therefore, in the direct neighbourhood of the perylene positive ion dissolved in a strong acid there cannot be another paramagnetic particle with which the ion could frequently interact.

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[10] Mackor and Gaaf, unpublished results.

In the weakly acidic solvents oxygen is expected to form O_2^- in the ion pair $M^+\cdot O_2^-$. Apparently the line width of its spectrum is so great that it is not observed. It may be noted that the spectrum of radicals produced from a hydrogen peroxide glass and attributed to $HO_2\cdot$ has a line width of about 100 gauss.[11] Bennett *et al.*[12] found that the spectrum of O_2^- in superoxide is even very much wider.

In conclusion, our results indicate that in acidic solvents aromatic hydrocarbons may react with molecular oxygen to form the hydrocarbon monopositive ion. In relatively weak acids the reaction takes place by an electron-transfer in the weak complex M,O_2 (eqn. 2). The ease of transfer depends primarily on (*a*) the ionization potential of the molecule, which is very low for perylene, and (*b*) the stabilization of the complex by interaction with the protons of the acid HZ. Our results give no information whether the acid transfers a proton to the O_2^- ion in the complex $M^+\cdot O_2^-$($M + O_2 + HZ \rightleftarrows M^+\cdot O_2HZ^-$) or whether the complex $M^+\cdot O_2^-$ is stabilized by solvation by the acid.

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[11] Livingston, Ghormley, and Zeldes, *J. Chem. Phys.*, 1956, **24**, 483; Gibson, Symons, and Townsend, *J.*, 1959, 269.

[12] Bennett, Ingram, Symons, George, and Griffith, *Phil. Mag.*, 1955, **46**, 443.